



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C03C 13/00		A1	(11) International Publication Number: WO 95/29135 (43) International Publication Date: 2 November 1995 (02.11.95)
<p>(21) International Application Number: PCT/EP95/01414</p> <p>(22) International Filing Date: 12 April 1995 (12.04.95)</p> <p>(30) Priority Data: PCT/EP94/01215 19 April 1994 (19.04.94) WO (34) Countries for which the regional or international application was filed: 9426429.8 30 December 1994 (30.12.94) GB </p> <p>(71) Applicant (for all designated States except US): ROCKWOOL INTERNATIONAL A/S [DK/DK]; Hovedgaden 584, DK-2640 Hedehusene (DK).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only): JENSEN, Soren, Lund [DK/DK]; Rudesovej 11, DK-2840 Holte (DK), CHRISTENSEN, Vermund, Rust [DK/DK]; Soager 11, DK-4000 Roskilde (DK).</p> <p>(74) Agent: GILL JENNINGS & EVERY; Broadgate House, 7 Eldon Street, London EC2M 7LH (GB).</p>		<p>(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).</p> <p>Published With international search report.</p>	

(54) Title: MAN-MADE VITREOUS FIBRE WOOL

(57) Abstract

The production and physiological dissolution rate of mineral wool formed of MMV fibres containing 35-66 % SiO₂, up to 10 % Al₂O₃, 10-45 % CaO, 2-30 % MgO, up to 10 % FeO, 0-7 % Na₂O + K₂O and 0-10 % TiO₂ is improved by including both P₂O₅ and B₂O₃ in the composition.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

MAN-MADE VITREOUS FIBRE WOOL

The present invention relates to man-made vitreous fibre (MMVF) wool containing iron and a relatively high amount of alkaline earth metals, and a low amount of alkali metals, conventionally known as stone, slag or basalt wool.

Various types of MMV fibres are known.

It is known, in the manufacture of traditional glass fibres, to include in the glass melt components which provide boron oxide (borate). This can improve the glass and the glass melt. However, borate-containing raw materials are expensive and are normally not added at all if possible, especially when the product contains iron and has low alkali and high alkaline earth content, as in conventional rock, stone and slag melts.

Glass wool products usually have a relatively high content of alkali metal (often above 13% Na₂O + K₂O). In this specification all analyses are expressed by weight of total composition measured as oxides. Glass filament and glass wool are usually free of iron but often also contain boron. Typically they contain less than 7% Al₂O₃. However E-Glass is a filamentary or other non-wool product and can have high aluminium and low or zero alkali metal. For instance JP-A-50090719 describes an E-Glass containing 15-16% Al₂O₃, 9.5-10.5% B₂O₃ and 5% P₂O₅. It is free of iron and sodium.

Glass fibres are described in EP-A-9418 which can have a wide range of optional components including, inter alia, iron, boron and phosphorous. None of the exemplified compositions contain both boron and phosphorous and they all have above 13% alkali metal oxide.

WO93/07741 describes fibres containing 0 to 4% P₂O₅, above 13% Na₂O, and up to 8% Al₂O₃ for use in horticulture. B₂O₃ can be present but the total amount of impurities (including any B₂O₃ which is included) must be not above 1%.

Glass wool is described in EP-A-412878 which has high alkali metal content (above 13%) and which contains borate. It is free of iron. Phosphorous is an optional component.

It is included allegedly to improve solubility of the fibres.

We are concerned with improving the solubility of the fibres in those wools generally referred to as rock, stone, 5 slag or basalt wools and which typically contain iron, a low amount of aluminium (below 10%), a low amount of alkali metal (below 7%) and a significant amount of alkaline earth metal (above 12%).

It has been proposed that it would be desirable to 10 provide such wools in which the MMV fibres are soluble in a physiological medium, in particular lung fluid.

It is known that the composition of a fibre can significantly affect its solubility. For instance, it is illustrated in WO87/05007 that fibres having a low alumina 15 content, in particular alumina below 10% by weight of composition, have improved solubility in a physiological environment. It is also known that inclusion of phosphorus can improve solubility in the physiological medium. This has been illustrated in the case of stone wool fibres in 20 for instance EP-A-459,897. This discloses stone wool fibres which comprise 1 to 10% of phosphorus as P_2O_5 . This component is said to provide solubility in the physiological medium. It can be assumed that increasing the amount of phosphorous within this range increases 25 solubility.

During the manufacture of MMVF wool the components which are to form the fibres are melted in a furnace, such as an electric, shaft, tank or cupola furnace. This produces a melt which may then be fiberised. The melt 30 usually has a melting point of around 1,400 to 1,600°C and is thus heated to above this temperature in the furnace. It has been found that the inclusion of significant amounts of phosphorous in the melt can lead to some problems. For instance phosphorus may volatilise in the furnace, leading 35 to difficulties of controlling the composition. In particular increasing the amount of phosphorus can adversely influence melt viscosity and properties. It

increases the risk of the melt (which contains iron and little or no alkali metal and low aluminium) undergoing phase separation and crystallisation. This leads to the formation and accumulation of solid or slag material in or 5 on the apparatus being used for forming the melt and converting the melt to fibres, and can cause increased amount of shot formation during the fibre-formation process, reduced material efficiency and higher costs.

It would therefore be desirable to form MMVF wool 10 having solubility characteristics of the type which would be expected in such wool from the use of relatively high phosphorus content while avoiding the manufacturing problems associated with relatively high phosphorous contents.

15 These problems tend to increase as the content of phosphate in the melt increases. For instance difficulties may arise as the content of phosphate increases beyond 5%. It may be possible with some furnaces to use up to 10% phosphate but in general for processing purposes it is 20 undesirable to include more than this.

However, even at low levels of alumina, and in particular when it is not possible to provide a melt having very low levels of alumina, dissolution rates of the fibres 25 are not as high as may be desirable at these levels of phosphate.

Therefore it would be desirable to improve the solubility of MMV fibres in the physiological medium without the necessity for using amounts of phosphate which lead to processing problems.

30 Fibres containing phosphorus and boron are mentioned in WO94/23801, from which this application claims priority.

According to the invention there is provided MMVF wool formed of fibres formed from a composition comprising, by weight of oxides (with iron expressed as FeO):

35	SiO ₂	35-66%
	Al ₂ O ₃	up to 10%
	CaO	10-45%

MgO	2-30%
FeO	up to 10%
Na ₂ O + K ₂ O	0-7%
TiO ₂	0-10%

5 P₂O₅ + B₂O₃ and other elements - up to 20%
and which includes both P₂O₅ and B₂O₃.

We find surprisingly that the use of a phosphate- and borate-containing melt can give fibres with adequate physiological solubility produced from a melt which has a 10 combination of good processing, viscosity and temperature characteristics, especially when the amount of Al₂O₃ is low.

We find that an upper limit of 10% on the amount of phosphate assists in reducing manufacturing problems, especially phase separation. The amount is preferably 6% 15 or less and is usually below 5%. We find that inclusion of borate increases the physiological solubility of the fibres without the necessity for using larger amounts of phosphate, and allows the use of phosphate even in amounts below 5% whilst retaining adequate physiological 20 solubility. We also find that borate has the additional advantage that it improves the physical properties of the melt, in particular it assists in reducing the melting point of the melt so that the risk of phase separation is reduced.

25 We also find that the use of boron in phosphorus-containing fibres results in improved fibre properties. For instance tensile strength, modulus of elasticity and length to diameter ratio can be improved. Tensile strength can be >700 MPa. Fibre Modulus of Elasticity can be <150 30 GPa. Length to fibre ratio can be >700, especially when the fibres are made by a cascade spinner.

The melt viscosity of the composition at 1400°C is preferably 10-70 poise, preferably 15 to 30 poise.

35 The fibres preferably have a dissolution rate at pH 7.5 of at least 30nm/day, and preferably at least 50 or at least 60nm/day, when measured by the stationary set up

method described in Environmental Health Perspectives, Vol. 102, Supplement 5, October 1994, pages 83-86.

The wool of the invention may be provided in any known way. According to the invention we also provide a process 5 of production of MMVF wool formed of fibres having a composition as defined above,
the process comprising

- providing raw materials to give the composition,
- providing a furnace,
- 10 placing the raw materials in the furnace and heating them to a temperature between 1,400°C and 1,600°C to produce a melt,
- fiberising the melt, and
- collecting the fibres as a wool.

15 In this process we find all the advantages in processing characteristics discussed above. Preferably the wool of the invention are made by this process of the invention.

In the process of the invention the raw materials used 20 to produce the melt may be any known raw materials which give the constituents of the composition. For instance, raw materials which may be used include diabase, cement, clay, olivine sand, silica sand, waste foundry sand, rasoelite, colemanite and other boron-containing materials, 25 converter slag, blast-furnace slag, electric arc furnace slag, iron oxide, waste stone wool, waste asbestos, lime, soda, glass waste, dolomite, bauxite, iron silicate, kaoline, calcium phosphate, quartz sand and other known melt ingredients.

30 The melt composition and hence the composition of the produced fibres preferably comprises at least 45%, often at least 47 or 48%, SiO₂. The amount is usually below 64 or 65%, preferably below 60%. Often the amount of SiO₂ is from 53.5 to 64%.

35 The composition preferably has a low alumina content, generally below 6% and preferably below 4%. In general it is very expensive to provide raw materials which contain no

alumina at all, so Al_2O_3 is present to some extent, usually in amounts of at least 0.5%, although alumina amounts are generally kept as low as possible, preferably below 3 or 2%. Amounts of 1-4% are often suitable.

5 The composition usually comprises at least 5%, generally at least 10% and preferably at least 15% alkaline earth metal oxides (CaO and MgO). Generally the amount is not more than 50%. Preferably CaO is contained in amounts of between 10 and 35%. In some compositions amounts of 10-
10 20% are preferred but in others amounts of 15 to 30% are preferred. MgO is usually present in an amount of at least 1%, often 5 to 20%, preferably 7 to 20%. For instance it may be in the range 5-15%.

15 The composition contains iron, and the amount is up to 10% by weight of total composition, measured as FeO . Preferably iron is present in amounts of at least 0.5 or 1%. Amounts of up to 4% are often suitable but amounts may be up to 9 or 10%, e.g., in the range 6.5-9%.

20 The composition may comprise alkali metals (Na_2O and K_2O) in amounts of 0% up to 6% or 7%. In general Na_2O is present in amounts of 0% up to 4% and K_2O is present in amounts up to 2%. Usually each is present in an amount of at least 0.1%, but both are optional and can be omitted.

25 Phosphate is present in the composition, generally in amounts of between 0.5 and 10%, measured as P_2O_5 , and often in the range 3 to 6%. For processing purposes it is desirable to keep the amount of phosphate as low as possible whilst incorporating enough to give an adequate dissolution effect. Preferably the phosphate amount
30 is at least 0.5 but below 5% (e.g., up to 4.5%), more preferably below 4%. Usually it is at least 2% or 3%.

35 Borate is incorporated in useful amounts of up to 10%, measured as B_2O_3 . The amount is preferably above 0.5 or 1%. In general, enough should be added to increase suitably the physiological dissolution rate, but incorporation of large amounts of borate necessitates the use of very expensive raw materials. Amounts of borate below 5% (e.g., 4.5 and

below) can give good results at economic cost but amounts up to 7 or 8% are sometimes preferred. The amount must be sufficient to give a useful effect and so is normally above 0.5 or 1% and preferably it is at least 3%. The amount of 5 B_2O_3 is usually below the amount of P_2O_5 for reasons of economy.

10 TiO_2 is optional. If present, its amount is usually 0.1 to 2%. The melt composition may additionally comprise 0 to 20% of other ingredients, for instance BaO , ZnO , ZrO_2 , F_2 , MnO , Li_2O , SrO . The total amount of other ingredients 15 is usually not more than 5%, or at most 10%.

The composition of the melt and of the fibres particularly preferably comprises:

15 SiO_2 45-64%, preferably 47-60 or 48-60%

Al_2O_3 0.5 to 4%

CaO 10-35%,

MgO 5-20%, preferably 5-15 or 7-15%

FeO 1-10%, preferably 1 to 9%

Na_2O 0 to 4%

20 K_2O 0 to 2%

TiO_2 0 to 2%

P_2O_5 at least 0.5% but preferably below 5%

B_2O_3 at least 0.5% but preferably below 5%

other elements 0 to 5%

25 all percentages being by weight of total composition and iron oxides being measured as FeO .

The raw materials are placed in a furnace where they are heated to a temperature between 1,400°C and 1,600°C in order to produce a melt. In general, they are heated to at 30 least 1,450°C, preferably between 1,450 and 1,540°C, generally around 1,480°C to 1,520°C.

The furnaces which can be used in the invention for forming the melt which is to be fiberised include cupola furnaces, oil and/or gas fired shaft or tank furnaces or 35 electric furnaces. In these furnaces the invention is particularly advantageous, although the composition also

shows advantages when using other known types of furnace. Preferred furnaces are those in which significant amounts of air are drawn. Slag formation and any volatilisation problems can be minimised by the invention.

5 The melt is fiberised in any known manner. In particular it may be fiberised by pouring into a fast-rotating cup having a substantially horizontal base and perforated side walls out of which is thrown as fibres, or by pouring onto one or more spinning wheels. The or each 10 wheel is mounted on a separate horizontal axis. Melt poured onto the circumference of the spinning wheel is flung off as fibres. Although a single wheel can be used, preferably a cascade system is used in which the melt is poured onto the top rotor of a set of rotating rotors each 15 mounted about a different substantially horizontal axis and arranged such that the melt is thrown from the top rotor onto the subsequent rotor, or on each subsequent rotor in sequence, in the set so as to throw mineral fibres off the or each subsequent rotor into a collection chamber. Any 20 apparatus known for the fiberisation of mineral melts to form wool may be used but a particularly preferred apparatus is described in our patent publication WO92/06047.

The fibres may then be collected as web or batt. The 25 web may be cross-lapped to form a batt. The batt may be consolidated into the desired MMVF wool product in known manner.

Binder is usually included in the batt. For instance it may be sprayed into the fibres before they are collected 30 as a web or batt.

The wool may be in the form of shaped batts or other elements or it may be in the form of tufts or granulates of mineral wool fibres, or in the form of articles made from such tufts or granulates.

35 The MMVF wool may be used for any of the conventional purposes of MMVF wool, for instance as a horticultural

growing medium, for sound or heat insulation and protection, for fire resistance and protection and as a filler or reinforcement.

The following are examples of suitable compositions,
5 (determined by X-ray fluorescence analysis and measured as weight %) and their dissolution rate at pH 7.5 in nm per day. Each composition can be melted in a cupola furnace and fiberised as in WO92/06047.

Compositions 1, 2, 3 and 4 are within the invention
10 while 1A, 1B, 2A, 3A and 4A are approximate comparisons and show that omitting the boron reduces dissolution rate. The comparative, borate free, compositions tend to slag formation, especially with the higher phosphorous contents.

Compositions	SiO ₂	Al ₂ O ₃	TiO ₂	FeO	CaO	MgO	Na ₂ O	K ₂ O	B ₂ O ₃	P ₂ O ₅	Dissolution Rate pH 7.5
1	53,4	3,6	0,5	2,5	16,9	10,1	3	0,5	5,1	3,2	65,5
1A	56,4	3,5	0,5	1,8	19,7	10,7	4,3	0,5	0	2,8	40,3
1B	54,6	4,3	0,6	2,8	15,6	10,6	4,7	0,6	0	1,3	8,6
2	58,1	3,3	0,5	2,1	18,9	10,3	3,4	0,5	3,2	2,5	53,9
2A	56,4	3,5	0,5	1,8	19,7	10,7	4,3	0,5	0	2,8	40,3
3	47,8	1	0,1	1,1	33,2	8,3	0,1	0,1	2,2	4	54,8
3A	46,9	2,4	0,4	1,3	32	9,2	0,1	0,5	0	6	23,8
4	54,2	2,4	0,1	3,9	21,2	8,2	0,1	0,3	5,9	2,2	57,9
4A	53,2	3,2	0,1	7,3	23,4	5,3	0,1	0,3	0	3,6	16,7

CLAIMS

1. Mineral wool formed of MMV fibres having a composition, expressed as oxides by weight of total composition, which is

5	SiO ₂	35-66%
	Al ₂ O ₃	up to 10%
	CaO	10-45%
	MgO	2-30%
	FeO	up to 10%
10	Na ₂ O + K ₂ O	0-7%
	TiO ₂	0-10%
	P ₂ O ₅ + B ₂ O ₃ and other elements up to 20%	
	and which includes both P ₂ O ₅ and B ₂ O ₃ .	
2. A wool according to claim 1 in which Al₂O₃ is up to 4% and each of P₂O₅ and B₂O₃ is up to 10%.
3. A wool according to claim 1 or claim 2 in which SiO₂ is 53.5 to 65%, CaO is 10-30%, MgO is 5 to 20%, and FeO is up to 9%.
4. A wool according to claim 1 in which the composition includes

20	SiO ₂	53.5-64% by weight
	Al ₂ O ₃	up to 4% by weight
	CaO	10-20% by weight
	MgO	10-20% by weight
25	FeO	6.5-9% by weight
	P ₂ O ₅ + B ₂ O ₃ up to 20% by weight and each is up to 10%.	
5. A wool according to claim 1 in which the composition includes

30	SiO ₂	53.5-65% by weight
	Al ₂ O ₃	up to 4% by weight
	CaO	15-30% by weight
	MgO	5-15% by weight
	FeO	up to 4% by weight
	P ₂ O ₅ + B ₂ O ₃ up to 20% by weight and each is up to 10%.	
35. 6. A wool according to claim 1 in which the composition includes P₂O₅ and B₂O₃ and

	SiO ₂	45 to 60%
--	------------------	-----------

	Al_2O_3	0.5 to 4%
	CaO	10 to 35%
	MgO	5 to 15%
	FeO	1 to 10%
5	Na_2O	0 to 4%
	K_2O	0 to 2%
	TiO_2	0 to 2%
	other elements	0 to 5%

7. A wool according to any preceding claim including P_2O_5 in an amount of 1 to 5% and B_2O_3 in an amount of 1 to 10%, preferably 1 to 5%.
- 10 8. A wool according to any preceding claim in which the amount of P_2O_5 is 0.5 to 4.5% and/or the amount of B_2O_3 is 0.5 to 4.5%.
- 15 9. A wool according to any preceding claim having a dissolution rate at pH 7.5 of at least 30nm/day.
10. A process of production of MMVF wool as defined in any preceding claim comprising
 - providing raw materials to give the composition,
 - 20 providing a furnace,
 - heating the raw materials in the furnace to a temperature between 1,400°C and 1,600°C to provide a melt
 - fiberising the melt, and collecting the fibres as wool.
- 25 11. A process according to claim 9 in which the furnace is a cupola furnace.

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C03C13/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 009 418 (OY PARTEK AB) 2 April 1980 cited in the application see claim 1 ---	1-11
A	DATABASE WPI Section Ch, Week 7710 Derwent Publications Ltd., London, GB; Class F, AN 77-16933Y & JP,A,50 090 719 (NIHON MUKI ZAIRYO) , 21 July 1975 cited in the application see abstract ---	1-11
A	EP,A,0 247 817 (PFIZER INC.) 2 December 1987 see page 2, line 58 - page 3, line 12 ---	1-11
		-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search

3 August 1995

Date of mailing of the international search report

17.08.95

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Van Bommel, L

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 412 878 (ISOVER SAINT-GOBAIN) 13 February 1991 cited in the application see page 2, line 34 - page 3, line 26 -----	1-11

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 95/01414

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0009418	02-04-80	JP-A-	55047246	03-04-80
EP-A-0247817	02-12-87	AU-A-	3720389	12-10-89
		AU-B-	6897294	20-10-94
		AU-A-	7345387	03-12-87
		AU-A-	8999091	13-02-92
		CA-A-	1265165	30-01-90
		JP-A-	62288137	15-12-87
		US-A-	4830989	16-05-89
EP-A-0412878	13-02-91	FR-A-	2650821	15-02-91
		FR-A-	2658182	16-08-91
		AU-B-	630484	29-10-92
		AU-A-	6002590	14-02-91
		CA-A-	2022446	12-02-91
		CN-A,B	1049834	13-03-91
		CN-A-	1093066	05-10-94
		DE-D-	69007369	21-04-94
		DE-T-	69007369	13-10-94
		ES-T-	2053139	16-07-94
		JP-A-	3093650	18-04-91
		PL-B-	165859	28-02-95
		SI-A-	9011548	31-12-94
		US-A-	5108957	28-04-92
		US-A-	5250488	05-10-93